(19) JAPANESE PATENT OFFICE

PATENT ABSTRACTS OF JAPAN

(11) Publication number: **05183189 A**

(43) Date of publication of application: **23.07.93**

(51) Int. Cl **H01L 33/00**
H01L 21/205
H01L 21/324

(21) Application number: **03357046**

(22) Date of filing: **24.12.91**

(30) Priority: **08.11.91 JP 03321353**

(71) Applicant: **NICHIA CHEM IND LTD**

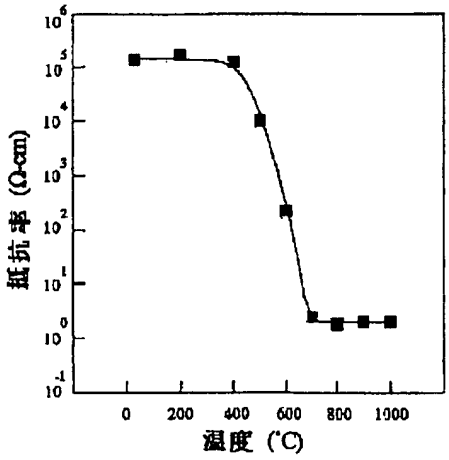
(72) Inventor: **NAKAMURA SHUJI**
IWASA SHIGETO

(54) **MANUFACTURE OF P-TYPE GALLIUM NITRIDE BASED COMPOUND SEMICONDUCTOR**

(57) Abstract:

PURPOSE: To provide a method for manufacturing a p-type gallium nitride based compound semiconductor, by which a gallium nitride based compound semiconductor doped with a p-type impurity is made a p-type semiconductor having a low resistance and further, the value of the resistance is made uniform over the whole of its wafer independently of its film thickness and moreover, a light emitting element made of the compound semiconductor can have a double or single hetero-structure.

CONSTITUTION: By a vapor growth method, a gallium nitride based compound semiconductor layer doped with a p-type impurity is formed, and thereafter, its annealing is performed at a temperature not lower than 400°C. However, it is more preferable that the annealing is performed in a pressurized atmosphere or performed by providing newly a cap layer on the gallium nitride based compound semiconductor.



[Claim(s)]

[Claim 1] The manufacture approach of p mold gallium nitride system compound semiconductor characterized by performing annealing at the temperature of 400 degrees C or more after forming the gallium nitride system compound semiconductor which doped p mold impurity by vapor growth.

[Claim 2] Said annealing is the manufacture approach of p mold gallium nitride system compound semiconductor according to claim 1 characterized by carrying out in the nitrogen-gas-atmosphere mind pressurized more than the decomposition pressure of the gallium nitride system compound semiconductor in the annealing temperature.

[Claim 3] The manufacture approach of claim 1 characterized by forming a cap layer further on the gallium nitride system compound semiconductor which doped said p mold impurity thru/or p mold gallium nitride system compound semiconductor given in 2.

[Claim 4] said cap layer -- GaXAl1-XN (however, 0<=X<=1), and AlN and Si3 -- the manufacture approach of p mold gallium nitride system compound semiconductor according to claim 3 characterized by consisting of a gap chosen from N4 and SiO2, or a kind of ingredient.

[Detailed Description of the Invention]

[0001]

[Industrial Application] the gallium nitride system compound semiconductor layer which this invention required for the manufacture approach of p mold gallium nitride system compound semiconductor used for luminescence devices, such as ultraviolet, a blue luminescence laser diode, ultraviolet, and a blue light emitting diode, doped p mold impurity by vapor growth in detail, and was formed -- low -- it is related with the approach of using as p mold [****].

[0002]

[Description of the Prior Art] Research is advanced using an II-VI group's ZnSe, an IV-IV group's SiC, an III-V group's GaN, etc., it is announced that luminescence which a gallium nitride system compound semiconductor [GaXAl1-XN (however, 0<=X<=1)] is ordinary temperature, and was comparatively excellent also in it is shown recently, and the blue

light emitting device attracts attention. The blue light emitting device which has the gallium nitride system compound semiconductor has the structure where the laminating of the epitaxial layer of the gallium nitride system compound semiconductor by which a general formula is fundamentally expressed with GaXAl1-XN (however, 0<=X<=1) on the substrate which consists of sapphire was carried out to n mold and i mold, or p mold at order.

[0003] It considers as the approach of carrying out the laminating of the gallium nitride system compound semiconductor, and vapor growth, such as organometallic compound vapor growth (henceforth the MOCVD method) and a molecular beam epitaxy method (henceforth the MBE method), is known well. When the approach using the MOCVD method is explained briefly, for example, this approach In the reaction container which installed silicon on sapphire, as reactant gas Organometallic compound gas {trimethylgallium (TMG), Supply}, such as trimethylaluminum (TMA) and ammonia, and crystal growth temperature is held to an about 900 degrees C - 1100 degrees C elevated temperature. It is the approach of carrying out the laminating of the gallium nitride system compound semiconductor to n mold, i mold, or p mold, growing up a gallium nitride system compound semiconductor on a substrate, and supplying other impurity gas if needed. Although there are SiC, Si, etc. in a substrate other than sapphire, generally sapphire is used. Although Si (however, in the case of a gallium nitride system compound semiconductor there is a property which becomes n mold even if it does not dope n mold impurity.) is well known as an n mold impurity and Zn, Cd, Be, Mg, calcium, Ba, etc. are mentioned as a p mold impurity, Mg and Zn are best known also in it.

[0004] Moreover, if a direct gallium nitride system compound semiconductor is grown up on silicon on sapphire at an elevated temperature, since the surface state and crystallinity will get remarkably bad as one of the formation approaches of the gallium nitride system compound semiconductor by the MOCVD method, before growing up at an elevated temperature, it is shown clearly by forming the buffer layer which consists of AlN and growing up at an elevated temperature on a buffer layer continuously by the low temperature around 600 degrees C first that crystallinity is markedly alike and improves (JP,2-229476,A). Moreover, this invention person showed that the laminating of the

crystalline gallium nitride system compound semiconductor excellent in the direction which makes GaN a buffer layer could be carried out rather than the conventional approach of making AlN a buffer layer in Japanese Patent Application No. No. 89840 [three to].

[0005] However, the blue luminescence device which has a gallium nitride system compound semiconductor has not yet resulted in utilization. because, a gallium nitride system compound semiconductor -- low -- it is because it is not made to p mold [****], so terrorism is impossible to double and it is not impossible of the light emitting device of much structures, such as terrorism, to a single. the gallium nitride system compound semiconductor obtained even if it grew up the gallium nitride system compound semiconductor which doped p mold impurity by vapor growth -- p mold -- not becoming -- resistivity -- 108 or more ohm-cm -- high -- the actual condition became a half-insulating material [****], i.e., i mold. For this reason, only the thing of the so-called metal-insulator-semiconductor structure to which structure of current and a blue light emitting device was used as the buffer layer and n type layer on the substrate, and used the laminating of the i type layer to order on it is known.

[0006]

[Problem(s) to be Solved by the Invention] high -- in JP,2-257679,A, Mg was doped as a p mold impurity as a means for forming i mold [****] into low resistance, and bringing close to p mold -- high -- after forming i mold nitriding gallium compound semi-conductor [****] in the maximum upper layer, the technique which forms about 0.5-micrometer layer into low resistance from a front face is indicated by irradiating an electron ray with an acceleration voltage of 6kV - 30kV on the front face. However, by this approach, since the whole wafer had to be irradiated only the penetration depth of an electron ray, i.e., a pole front face, being able to carry out [low ****]-izing, and scanning an electron ray, the problem that-izing could not be carried out [low ****] was in the homogeneity within a field.

[0007] therefore, the gallium nitride system compound semiconductor with which the purpose of this invention doped p mold impurity -- low -- it considers as p mold [****], and is not further based on thickness, but the manufacture approach of p mold gallium nitride system compound semiconductor that resistance is uniform to the whole wafer, and

it can do with terrorism to double and it can do a light emitting device to a single with the structure in which terrorism structure is possible is offered.

[0008]

[Means for Solving the Problem] After the manufacture approach of p mold gallium nitride system compound semiconductor of this invention forms the gallium nitride system compound semiconductor layer which doped p mold impurity by vapor growth, it is characterized by performing annealing at the temperature of 400 degrees C or more.

[0009] After it forms the gallium nitride system compound semiconductor layer which doped p mold impurity, annealing (Annealing: annealing) may be performed within a reaction container, may pick out a wafer from a reaction container and may perform it using the equipment only for annealing. An annealing ambient atmosphere is performed among a vacuum in inert gas, such as N2, helium, Ne, and Ar, or these mixed-gas ambient atmospheres, and is most preferably performed in the nitrogen-gas-atmosphere mind pressurized above the decomposition pressure of the gallium nitride system compound semiconductor in annealing temperature. It is because there is an operation which prevents that N in a gallium nitride system compound semiconductor decomposes and goes away during annealing by pressurizing as a nitrogen-gas-atmosphere mind.

[0010] For example, in GaN, the decomposition pressure of GaN is at about 1 atmospheric pressure and 1100 degrees C in about 0.01 atmospheric pressures and 1000 degrees C by 800 degrees C as about 10 atmospheric pressures. For this reason, in case annealing of the gallium nitride system compound semiconductor is carried out above 400 degrees C, disassembly of a gallium nitride system compound semiconductor occurs to some extent, and it is in the inclination for that crystallinity to worsen. Therefore, decomposition can be prevented by pressurizing with nitrogen as mentioned above.

[0011] annealing temperature -- 400 degrees C or more -- desirable -- 700 degrees C or more -- it is -- 1-minute or more maintenance -- it carries out by holding 10 minutes or more preferably. Even if it carries out above 1000 degrees C, by pressurizing with nitrogen, as described above, it is stabilized so that decomposition can be prevented and it may state later, and crystalline outstanding p mold gallium nitride system compound semiconductor is obtained.

[0012] Moreover, as a means to suppress disassembly of a gallium nitride system compound semiconductor under annealing, annealing may be performed, after making a cap layer form further on the gallium nitride system compound semiconductor layer which doped p mold impurity. without it makes a gallium nitride system compound semiconductor disassemble into reduced pressure and ordinary pressure by carrying out annealing above 400 degrees C after being a cap layer, i.e., a protective coat, and forming it on the gallium nitride system compound semiconductor which doped p mold impurity to say nothing of the bottom of pressurization -- low -- it can consider as p mold [****].

[0013] In order to form a cap layer, after forming the gallium nitride system compound semiconductor layer which doped p mold impurity, you may form within a reaction container continuously, and a wafer may be picked out from a reaction container and you may form, other crystal growth equipment, for example, plasma-CVD equipment etc., etc. if it is the ingredient which can be formed on a gallium nitride system compound semiconductor as an ingredient of a cap layer and is a stable ingredient above 400 degrees C -- what kind of thing -- ****** -- desirable -- GaXAl1- XN (however, 0<=X<=1) and Si3 -- N4 and SiO2 can be mentioned and the class of ingredient is suitably chosen with annealing temperature. Moreover, the thickness of a cap layer is usually formed by the thickness of 0.01-5 micrometers. Since the effectiveness as a protective coat fully not being acquired if thinner than 0.01 micrometers, and removing a cap layer by etching after annealing if thicker than 5 micrometers, and exposing p mold gallium nitride system compound semiconductor layer takes time and effort, it is not economical.

[0014]

[Function] the gallium nitride system compound semiconductor layer in which drawing 1 doped p mold impurity -- annealing -- low -- it is drawing showing changing to p mold [****]. After it takes out a wafer, changes temperature, after this forms a GaN layer by 4-micrometer thickness, forming a GaN buffer layer first on silicon on sapphire, and doping Mg as a p mold impurity on it using the MOCVD method, and it performs annealing for 10 minutes in nitrogen-gas-atmosphere mind, it is drawing which performed hole measurement of a wafer and plotted resistivity as a function of annealing temperature.

[0015] the resistivity of the GaN layer which doped Mg rapidly [as shown in this

drawing] from the hit exceeding 400 degrees C -- decreasing -- about 1 law from 700 degrees C or more -- low -- p mold property [****] was shown and the effectiveness of annealing has shown up. In addition, the GaN layers after annealing were resistivity 2 ohm-cm and 2x1017/of hole carrier concentration cm 3 to the GaN layers before annealing of the hole measurement result of the GaN layer which carried out annealing to the GaN layer which does not carry out annealing above 700 degrees C having been resistivity 2x105 ohm-cm and 8x1010/of hole carrier concentration cm 3. Moreover, although this drawing was drawing having shown GaN, it was confirmed that the same result is obtained also in GaXAl1-XN (0<=X<1) which similarly doped p mold impurity.

[0016] Furthermore, as a result of etching the 4 above-mentioned micrometers GaN layer which carried out annealing at 700 degrees C, making it the thickness of 2 micrometers and performing hole measurement, it was 2x1017/of hole carrier concentration cm 3, and resistivity 3 ohm-cm, and was the almost same value as etching before. namely, the GaN layer which doped p mold impurity -- annealing -- the depth direction homogeneity -- all fields -- crossing -- low -- it had become p mold [****].

[0017] The wafer in which the GaN buffer layer and the 4-micrometer GaN layer which doped Mg were formed on silicon on sapphire is used using law. moreover, drawing 2 -- the same -- MOCVD -- The wafer which performed annealing for [in nitrogen-gas-atmosphere mind] 20 minutes at 1000 degrees C, and was performed under the pressurization of 20 atmospheric pressures (a), helium-Cd laser is irradiated as the excitation light source at the p mold GaN layer of the wafer (b) performed with atmospheric pressure, respectively. It is drawing comparing and showing crystallinity by the photoluminescence reinforcement, and it can be estimated that crystallinity is excellent, so that the blue luminescence reinforcement in 450nm of the photoluminescence is strong.

[0018] Although it is in the inclination for the crystallinity to worsen when a GaN layer pyrolyzes when annealing is performed at an elevated temperature 1000 degrees C or more as shown in drawing 2 , by pressurizing, a pyrolysis can be prevented and the outstanding crystalline p mold GaN layer is obtained.

[0019] Moreover, the wafer with which drawing 3 similarly formed the GaN buffer layer and the 4-micrometer GaN layer which doped Mg on silicon on sapphire (c), The wafer (d)

which furthermore grew up the AlN layer by 0.5-micrometer thickness as a cap layer on it is shortly set in atmospheric pressure. After performing annealing for 20 minutes by 1000 degrees C and nitrogen-gas-atmosphere mind, it is drawing comparing and showing the crystallinity of the p mold GaN layer which removed the cap layer by etching and was exposed by photoluminescence reinforcement similarly.

[0020] As shown in drawing 3 , since decomposition of a p mold GaN layer will progress if the p mold GaN layer (c) which performed annealing, without growing up a cap layer becomes annealing in an elevated temperature, the luminescence reinforcement in 450nm will become weak. However, although AlN of a cap layer is decomposed by growing up a cap layer (AlN in this case), since a p mold GaN layer does not decompose, luminescence reinforcement is still strong.

[0021] annealing -- low -- it is guessed that the reason p mold gallium nitride system compound semiconductor [****] is obtained is as follows.

[0022] That is, in growth of a gallium nitride system compound semiconductor layer, as a source of N, generally NH3 is used and it is thought that this NH3 decomposes during growth and atomic hydrogen is made. It is thought by combining with Mg with which this atomic hydrogen was doped as acceptor impurity, Zn, etc. that the impurity is prevented from p mold working as an acceptor, such as Mg and Zn. For this reason, the gallium nitride system compound semiconductor which doped p mold impurity after a reaction shows high resistance.

[0023] in order [however,] to dissociate thermally the hydrogen combined in forms, such as Mg-H and Zn-H, by performing annealing after growth, to go away from the gallium nitride system compound semiconductor layer which doped p mold impurity and for p mold impurity to work as an acceptor normally -- low -- p mold gallium nitride system compound semiconductor [****] is obtained. Therefore, it is not desirable to use the gas which contains the hydrogen atom of NH3 and H2 grade in an annealing ambient atmosphere. Moreover, in a cap layer, it is not desirable to use the ingredient containing a hydrogen atom at the above reason.

[0024]

[Example] This invention is explained in full detail in the example below.

[Example 1] The silicon on sapphire washed well first is installed in the susceptor in a reaction container. After carrying out evacuation of the inside of a container, a substrate is heated for hydrogen gas for 20 minutes at 1050 degrees C with a sink, and a surface oxide is removed. then, temperature -- 510 degrees C -- cooling -- 510 degrees C -- setting -- as the source of Ga -- TMG gas -- as a part for 27x10 -six-mol/, and the source of N -- ammonia gas -- as 4.0l. a part for /and carrier gas, hydrogen gas is grown up by part for 2.0l./, and a GaN buffer layer is grown up by 200A thickness with a sink.

[0025] Next, after stopping only TMG gas and raising temperature to 1030 degrees C, TMG gas newly grows up Cp2Mg (magnesium cyclopentadienyl) gas for 60 minutes with a sink by part for 3.6x10 -six-mol/by 54x10 -six-mol/again, and the GaN layer which doped Mg is grown up by 4-micrometer thickness.

[0026] The wafer into which the above was grown up was picked out from the reaction container after cooling, and it put into annealing equipment, it held for 20 minutes at 800 degrees C in ordinary pressure and nitrogen-gas-atmosphere mind, and annealing was performed.

[0027] As a result of performing hole measurement of the p mold GaN layer obtained by carrying out annealing, the resistivity of 2ohms and cm, and 2x1017/of hole carrier concentration cm 3 and outstanding p mold property were shown.

[0028] In the [example 2] example 1, after growing up a Mg dope GaN layer, Cp2Mg gas is stopped, and a GaN layer is continuously grown up by 0.5-micrometer thickness as a cap layer.

[0029] In annealing equipment, annealing is performed for 20 minutes at 800 degrees C among the mixed-gas ambient atmosphere of nitrogen and an argon under ordinary pressure like an example 1. Then, as a result of having removed the 0.5-micrometer layer from the front face, removing a cap layer, exposing a p mold GaN layer and performing hole measurement similarly by dry etching, resistivity 2 ohm-cm, and 1.5x1017/of carrier concentration cm 3 and outstanding p mold property were shown. In addition, the blue luminescence reinforcement of 450nm of photoluminescence was about 4 times stronger as compared with the example 1.

[0030] In the [example 3] example 1, after growing up a Mg dope GaN layer, a wafer is

picked out from a reaction container and annealing is performed for 20 minutes at 800 degrees C among 20 atmospheric pressures and nitrogen-gas-atmosphere mind in annealing equipment. As a result of performing hole measurement, resistivity 2 ohm-cm, and 2.0x1017/of carrier concentration cm 3 and outstanding p mold property were shown, and the luminescence reinforcement of 450nm of photoluminescence was about 4 times stronger as compared with the example 1.

[0031] After growing up a Mg dope GaN layer, a wafer is picked out from a reaction container and it forms SiO two-layer by 0.5-micrometer thickness as a cap layer on it in the [example 4] example 1 using plasma-CVD equipment.

[0032] In annealing equipment, annealing is performed for 20 minutes at 1000 degrees C among nitrogen-gas-atmosphere mind and atmospheric pressure. Then, as a result of removing a SiO2 cap layer by fluoric acid, exposing a p mold GaN layer and performing hole measurement similarly, resistivity 2 ohm-cm, and 2.0x1017/of carrier concentration cm 3 and outstanding p mold property were shown. Moreover, the luminescence reinforcement of 450nm of photoluminescence was about 20 times strong as compared with what did not form a cap layer but performed annealing on the same conditions.

[0033] In the [example 5] example 1, after growing up a Mg dope GaN layer, Cp2Mg gas newly grows up a stop and the n mold Ga0.9aluminum0.1N layer which passes TMA gas for 20 minutes and by which Si was doped [gas / part / for 2.2x10 -ten mol/] in 6x10 -six-mol part [for /] and SiH4 (mono silane) gas by the thickness of 0.8 micrometers succeedingly.

[0034] After cooling a stop, and hydrogen gas and ammonia gas for TMG gas, TMA gas, and SiH4 gas to a room temperature with a sink, a wafer is taken out, and it puts into annealing equipment, it holds for 20 minutes at 700 degrees C in nitrogen-gas-atmosphere mind, and annealing is performed.

[0035] Thus, the component of terrorism structure was made to the single by which the laminating of a p mold GaN layer and the n mold Ga0.9aluminum0.1N layer was carried out to order on silicon on sapphire. After having etched the n mold Ga0.9aluminum0.1N layer part for the gallium nitride system compound semiconductor layer of this component according to the conventional method, exposing a part of p mold GaN layer and attaching

an ohmic electrode to each layer, it cut in the shape of a chip with the dicing saw. The electrode was taken out from n type layer exposed on the chip, and p type layer, mold was carried out after that, and blue light emitting diode was produced. The property of this light emitting diode showed blue luminescence of 90 microwatts of radiant power outputs by 20mA of forward current, and forward voltage 5V, and peak wavelength was 430nm. This radiant power output is the high value which was not reported in the past as an output of blue light emitting diode.

[0036] When the light emitting diode which does not carry out annealing on the other hand, but has terrorism structure to the same single was manufactured, it was only shining with luminescence faintly appropriate for [this light emitting diode had forward voltage also about 60V in 20mA of forward current, and] yellow moreover, and it broke immediately and a radiant power output cannot be measured.

[0037] A GaN buffer layer is formed by 200A thickness on silicon on sapphire like the [example 6] example 1.

[0038] Next, after raising only TMG gas by the stop and raising temperature even at 1030 degrees C, the n mold GaN layer by which SiH4 (mono silane) gas was newly grown up for 60 minutes with the sink by part for 2.2x10 -ten-mol/with a part for 54x10 -six-mol/, and Si was doped in TMG gas is again grown up by 4-micrometer thickness.

[0039] Then, SiH4 gas grows up a stop and Cp2Mg gas for 30 minutes with a sink by part for 3.6x10 -six-mol/, and a Mg dope GaN layer is grown up by the thickness of 2.0 micrometers.

[0040] The gas which flows TMG gas and Cp2Mg gas in a reaction container in a stop, and hydrogen gas and ammonia gas after cooling to a room temperature with a sink is permuted by nitrogen gas, the temperature in a reaction container is raised to 1000 degrees C with a sink, nitrogen gas is held for 20 minutes within a reaction container, and annealing is performed.

[0041] Thus, when the obtained component was used as light emitting diode and made to emit light like an example 4, blue luminescence which has a luminescence peak near 430nm was shown, the radiant power output was 50 microwatts in 20mA, and, similarly forward voltage was 4V in 20mA. Moreover, when annealing is not performed, but the

component of the same structure is produced and it considers as light emitting diode, in 20mA, light was slightly emitted in yellow, and diode has broken immediately.

[0042]

[Effect of the Invention] as stated above, even if it dopes p mold impurity conventionally according to the manufacture approach of this invention -- low -- the gallium nitride system compound semiconductor used as p mold [****] -- low -- since it can consider as p mold [****], the component of much structures can be manufactured. Furthermore, although only the pole front face of the maximum upper layer was able to carry out [low ****]-izing by the approach by the conventional electron beam irradiation, in this invention, since-izing of the whole can be carried out [p mold], moreover,-izing of the gallium nitride system compound semiconductor layer in which p mold impurity was doped by annealing can be carried out [p mold] to the homogeneity within a field at the depth direction homogeneity, and, moreover, p type layer can be formed even in what layer. since [moreover,] the layer of a thick film can be formed -- high -- a brightness blue light emitting device can be obtained.

[Brief Description of the Drawings]

[Drawing 1] Drawing showing the annealing temperature by one example of this invention, and the relation of resistivity.

[Drawing 2] Drawing comparing and showing the crystallinity of the p mold GaN layer by one example of this invention by photoluminescence reinforcement.

[Drawing 3] Drawing comparing and showing the crystallinity of the p mold GaN layer by one example of this invention by photoluminescence reinforcement.